Extraction of Tantalum and Columbium From Their Ores

DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE OF COLUMBIA UNIVERSITY

BY

LESLIE G. JENNESS, B.S., M.S.

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NEW YORK CITY

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ACKNOWLEDGMENT.

The author wishes to express to Professor Colin G. Fink his most sincere thanks and appreciation for the encouragement and suggestions which were constantly given during the prosecution of this work.

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EXTRACTION OF TANTALUM AND COLUMBIUM FROM THEIR ORES.

By Leslie G. Jenness.

Abstract.

Tantalum and columbium possess valuable properties which distinguish them from other metals and, in spite of their high cost of production, demands for these metals have grown during recent years. One present difficulty which adds to the cost of the metals is the cost of extracting the oxides from the ore. The present methods, involving fusion processes, are tedious, costly and poorly adapted to commercial operation. The problem of extracting these metal oxides by a method which could be conducted economically on a large scale was undertaken, realizing that a solution of this problem would reduce the cost of these metals and create still further demands.

A method of leaching and recovering the salts and oxides directly from the solution appeared to be the simplest process for commercial application. It was certain, however, that common leaching solutions, such as used for copper and lead ores, would have no effect on these ores, as they are insoluble in most reagents. It was also evident that the leaching reagents must be capable of decomposing the ore, as well as acting as a solvent for tantalum and columbium oxides. It was known that hydrofluoric acid and carboxylic acids were solvents for tantalum and columbium oxides, and that hydrofluoric acid attacks the ore. It was discovered by us, however, that hydrofluoric acid was capable of decomposing the ore much more readily in the presence of a carboxylic acid, and that a leaching solution comprised of hydrofluoric acid and oxalic acid was far more effective than either used singly. An investigation was conducted, therefore, to determine the function of the carboxylic acids, the optimum concentration of reagents and conditions for leaching, the method of recovering the metal salts and oxides from solution, and the approximate cost of their production.

The investigations showed that the rate of decomposition of the ore was proportional to the hydrofluoric acid concentration, and that oxalic acid was a better solvent for tantalum and columbium oxides than hydrofluoric acid. Furthermore, the oxalic acid appeared to form poorly dissociated compounds of tantalum and columbium, and liberated hydrofluoric acid for further decomposing action on the ore. Acting together, therefore, the two acids were capable of both decomposing and dissolving the ore much more effectively than either acid alone, or than the two used successively. All carboxylic acids showed the same

effect as oxalic acid, but the efficiency of the acid decreased with increase in molecular weight.

It was found that the same amount of reagents could leach much more ore, when starting in large concentrations and diluting by steam condensation, than could be accomplished by leaching at constant volume at approximately the same temperature. Investigations showed that the rate of conversion of the tantalum and columbium from the fluoride to the oxalate was much slower than was the rate of decomposition of the ore to form the fluoride. It was impossible, therefore, to obtain the maximum benefit from the oxalic acid, as some hydrofluoric acid was always lost by volatilization. The nearest approach to the ideal conditions, however, was to start the leach in concentrated solutions, where the decomposing reaction was favored, and to dissolve the soluble compounds upon dilution. We found that the introduction of steam into the solution served as a means of both heating and diluting the solution and appeared to be the most simple manner of conducting the process commercially. The optimum concentration of leaching reagents was worked out for this method.

Slightly more than 60 per cent of the tantalum leached could be crystallized from the solution in the form of potassium tantalofluoride free from columbium salts. Part of this salt would require recrystallization to free it from oxalic acid, and a large amount of oxalic acid could be recovered.

The combined oxides of tantalum and columbium can be recovered from the solution by fractional precipitation with ammonium hydroxide, the tantalum and columbium precipitating while the solution is still acid.

Tantalite, columbite and samarskite ores were investigated. There is little difference between the action on tantalite and columbite. Samarskite is even more readily leached than the other two, and this method has a great advantage over other methods, since it leaves the rare earth metals in the gangue.

The cost of the materials for preparing the combined Ta and Cb oxides, based on semi-commercial results, is 82 cents per pound. Considering the recovery of 50 per cent of the oxalic acid, the cost of leaching the tantalum oxide is 63 cents per pound. It seems fair to estimate, therefore, that a good grade of tantalum oxide can be prepared at about $2.00 per pound, and should be in the class with tungstic oxide and other similar oxides. In view of the fact that it is difficult to procure any appreciable quantity of tantalum oxide on the market, even at a cost of $30 per pound, it would seem that our new leaching method warrants considerable consideration.

Tantalum and columbium occur together in tantalite and columbite ores, which may be considered as ferrotantalate ($FeTa_2O_6$), with part of the iron and tantalum replaced by manganese and columbium respectively, the general formula, therefore, becoming $(Fe, Mn)O.(Ta, Cb)_2O_5$. The ratio of tantalum to columbium is not fixed, and the amount of tantaulm may vary from one-third to three times that of columbium. Those minerals having a high content of tantalum are called tantalite, while those possessing larger amounts of columbium are classified as columbite ores. These minerals occur with veins of cassiterite and wolframite, and may contain small amounts of tin, tungsten, titanium and silica.

Several methods have been proposed for the extraction of tantalum and columbium from these ores, among which are:

(a) Fusion with potassium or sodium bisulfate. The finely ground ore is fused with potassium bisulfate, after which the mass is boiled with water and the fusion repeated several times. The residue finally resulting is digested with ammonium sulfide to remove traces of tin and tungsten, boiled with hydrochloric acid, filtered and washed. These oxides are then dissolved in hydrofluoric acid, the silica evolved as silicon tetrafluoride, and the hydrofluoric acid solution used for the potassium double fluoride separation of tantalum.

(b) Fusion with sodium carbonate and sodium nitrate.[1] This fusion renders the tantalum and columbium soluble, and they are extracted with a small quantity of soluble impurities. The tantalum, columbium and titanium are the only metals present which are precipitated from this solution by sulfur dioxide, thus enabling the separation of these metals from the balance of the ore. Weiss and Landecker[2] also suggest the separation of tantalum from the sodium tantalate and columbate solution by means of carbon dioxide, the tantalum being precipitated while the columbium remains soluble. Many workers[3] severely criticize this method, however, and state that it is not operable.

(c) Volatilization with chlorine. Cooper[4] states that tantalum, columbium and iron can be volatilized as chlorides by passing chlorine over the ore at 500° C. The chlorides are then hydrolyzed in a sodium chloride solution, to precipitate tantalic and columbic acids and retain the iron as soluble ferric chloride. It appears evident that Cooper used

[1] Wedekind and Maass, Z. angew. Chem., **23**, 2314 (1911).
[2] Weiss and Landecker, Z. anorg. Chem., **64**, 65 (1910).
[3] Hauser and Lewite, Z. angew. Chem., **25**, 100 (1912); Foote and Langley, Am. J. Sci., **30**, 401 (1911); Hahn and Gille, Z. angew. Chem., **112**, 283 (1920); Ruff and Schiller, Z. anorg. Chem., **72**, 329 (1912).
[4] H. S. Cooper, U. S. Patent 1,507,987, Sept. 9, 1924.

ferrotantalum for experimentation, as the ores cannot be appreciably volatilized under these conditions.

(d) Fusion with sodium hydroxide. The ore is fused with sodium hydroxide, the fused mass leached with sulfuric acid to dissolve manganese and iron, and the balance of the treatment continued as described in (a). This method is preferred to that of the bisulfate fusion, since it can be carried out in iron, and is probably the only method in commercial use at the present time.

It is evident from an inspection of these methods, as well as the prevailing price of tantalum oxide, that they are not readily adapted to commercial application. This has led to a study of the problem of leaching tantalum and columbium ores with the ultimate aim of simplifying the process and reducing the cost of extraction.

PRELIMINARY LEACHING RESULTS.

It was evident that a leaching solution for these ores must be capable of decomposing the ore, as well as acting as a solvent for tantalum and columbium. Hydrofluoric acid and carboxylic acids appear to be the only acids that dissolve tantalum oxide appreciably, and it was found that these acids were also capable of decomposing the ore, hydrofluoric acid being much more effective. When hydrofluoric and oxalic acids were used together, it was found that the ore was attacked much more readily than when the acids were used singly and an investigation was made to study: (1) The effect of carboxylic acids. (2) Optimum conditions for leaching. (3) Method of recovering tantalum and columbium from the solution after leaching. (4) Efficiency and cost of extraction.

MATERIALS.

The materials used for this work were of two classes. Baker's analyzed chemicals were used in making a study of the effect of carboxylic acids on the hydrofluoric acid leaching solution, while commercial chemicals were employed in studying the process on a larger scale of production. The calcium fluoride, used as a source of hydrofluoric acid, was the native ore, fluorspar. A 200-mesh tantalite ore was procured from the Foote Mineral Company, Philadelphia, with the following analysis:

	Per cent
Ta_2O_5	55.0
Cb_2O_5	22.4
SiO_2	10.0
TiO_2	0.39
SnO_2	2.29
Fe_2O_3	0.18
MnO_2	9.63

Combined Effect of Hydrofluoric and Oxalic Acids.

A series of leaches was made on 100 grams of tantalite ore, the charges consisting of:

(a) 100 grams 50 per cent HF.

(b) 310 grams $H_2C_2O_4.2H_2O$.

(c) 100 grams 50 per cent HF and 310 grams $H_2C_2O_4.2H_2O$.

(d) 100 grams CaF_2 and 200 cc. conc. H_2SO_4.

(e) 100 grams CaF_2 and 310 grams $H_2C_2O_4.2H_2O$.

(f) 100 grams CaF_2, 310 g. $H_2C_2O_4.2H_2O$ and 200 cc. H_2SO_4.

These leaches were conducted in a calibrated, lead-lined pail of eight liters capacity. Steam was admitted through a lead coil with small perforations in the lower turn, the condensation of the steam maintaining a temperature of about 95° C. Sufficient water was added to the charge to give a starting volume of 500 cc. The volume of the solution was increased, due to the condensation of the steam, as the leach continued, about four hours being required to bring the volume to six liters.

Samples were withdrawn at definite volumes of the leach, and analyzed for total oxides by precipitation with ammonium hydroxide. The results are expressed graphically in Fig. 1 in terms of ore leached, as it was also shown by analysis that the tantalum and columbium were present in the total oxides leached in nearly the same percentage as in the ore.

It would be expected, therefore, that the rate of leaching would be much greater over the initial period by the introduction of hydrofluoric acid, and that it would be greater over the final period when using calcium fluoride and sulfuric acid. It it also probable that some of the difference between these two curves is explained by the increased solubility of the tantalum and columbium compounds in the presence of strong acids.

Effect of Concentration of Oxalic Acid.

To determine the effect of varying concentrations of oxalic acid, leaches were conducted with one-half and one-quarter of the amount originally selected, 310 grams, the amount of calcium fluoride and sulfuric acid remaining constant. The results of these leaches are shown in Fig. 2.

In comparing the results, it is seen that the combined effect of hydrofluoric acid and oxalic acid is far greater than either used singly. This is probably due to the fact that hydrofluoric acid is a much better de-

composing agent for the ore while the oxalic acid acts as a much better solvent.

It is also evident that the rate of decomposition of the ore is largely dependent upon the concentration of hydrofluoric acid. This is shown by a comparison of the leach with hydrofluoric acid and that using calcium fluoride and sulfuric acid. The concentration of hydrofluoric acid will be much greater at the start in the former case, while its rate of volatilization, and consequently loss from solution, will be greater.

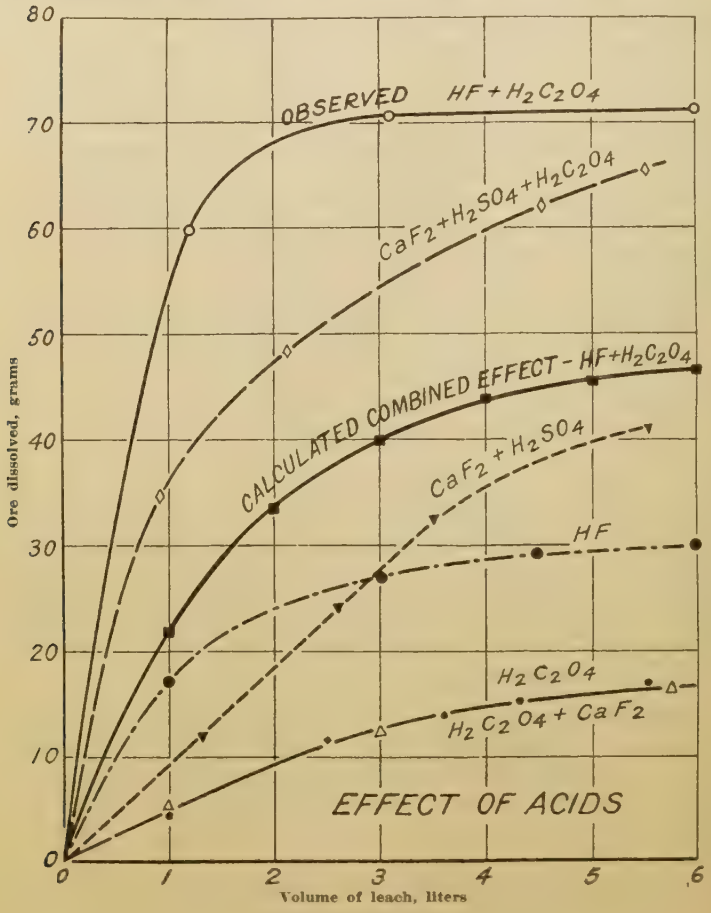

Fig. 1. Effect of acids.

From the curves of Fig. 2 it is noticed that when the amount of oxalic acid is reduced from 310 grams to 155 grams the quantity of ore leached remains the same until the volume reaches 2.5 liters, after which it gradually falls off. When the quantity of oxalic acid is again halved, the amount of ore leached diminishes quite markedly. It seems evident that an excess of oxalic acid, over that necessary to form

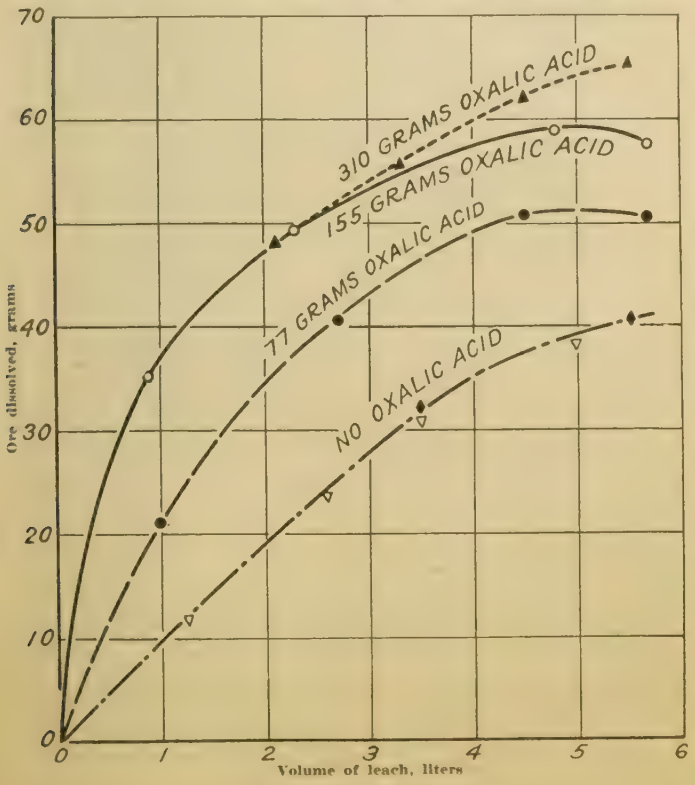

FIG. 2. Effect of oxalic acid.

the oxalate compounds, is necessary to hold the compounds in solution. This is also verified by Powell and Schoeller,[5] who have worked with a solution of ammonium oxalate and sulfuric acid as a solvent for tantalum and columbium oxides.

Since little improvement in leaching is shown by a solution containing more than 155 grams of oxalic acid, and since smaller quantities

[5] Powell and Schoeller, The Analyst, 50, 485 (1925).

show a decided drop in leaching efficiency, it is concluded that a final concentration of 30 grams per liter would constitute the most economically efficient leaching solution.

Effect of Other Carboxylic Acids.

After recognizing the beneficial effect of oxalic acid upon a hydrofluoric acid leaching solution for these ores, it seemed of value to de-

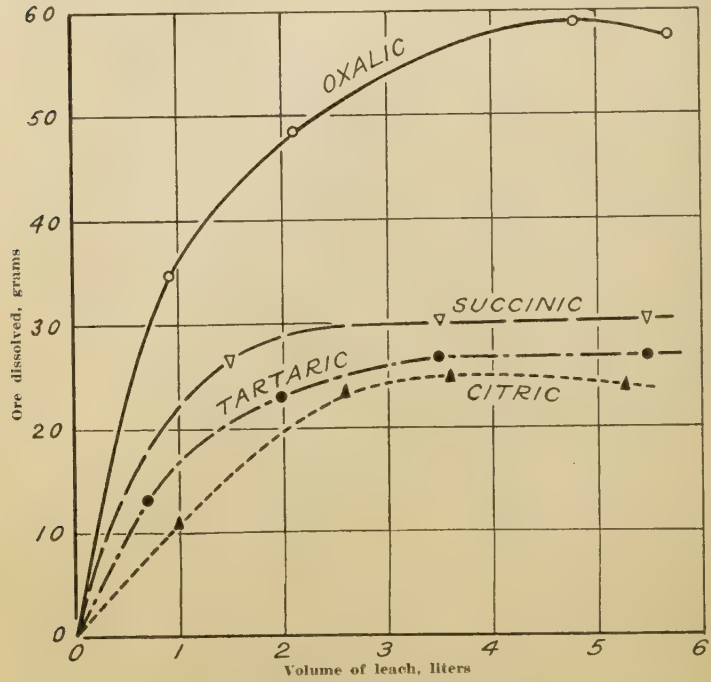

FIG. 3. Effect of carboxylic acids.

termine the definite cause for this effect. It was found that the presence of reducing gases, such as carbon monoxide and sulfur dioxide, did not produce the same effect as oxalic acid, and it was concluded that the results could not be attributed to any decomposition of the oxalic acid. Furthermore, the total amount of oxalate added was shown by analysis to be present after leaching was complete. It seemed, therefore, that its function must be that of a solvent and a study of other carboxylic acids was made.

To compare the action of other carboxylic acids with that of oxalic acid, a series of leaches was conducted using molecularly equivalent quantities of the other carboxylic acids. The leach obtained with 100 grams of calcium fluoride, 200 cc. sulfuric acid and 155 grams of oxalic acid was taken for comparison. Table I shows the molecularly equivalent quantities of other acids selected to replace the oxalic acid in successive leaches. The results obtained from the leaches are shown graphically in Fig. 3.

It was observed that all of the carboxylic acids increase the rate of solution of the ore in concentrated solutions, that is, during the initial part of the leach. It was of further interest to note that this property

TABLE I.

Acid	Formula as Taken	Molecular Weight		Weight Taken
		Cryst.	Anhyd.	
Oxalic	$\begin{matrix}COOH\\ \\ COOH\end{matrix}.2H_2O$	126	90	155
Succinic	$\begin{matrix}CH_2COOH\\ \\ CH_2COOH\end{matrix}$	118	118	145
Tartaric	$\begin{matrix}CH(OH)COOH\\ \\ CH(OH)COOH\end{matrix}$	150	150	185
Citric	$\begin{matrix}CH_2COOH\\ \\ CH(OH)COOH.H_2C\\ \\ CH_2COOH\end{matrix}$	210	192	258

decreased with an increase in the molecular weight of the acid, and that the presence of the hydroxyl group appeared to make no difference. These facts strongly indicated that the carboxylic group was the important factor in rendering the tantalum and columbium more soluble, and that oxalic acid was the desired form of introducing this group.

Comparison of Action on Columbite and Tantalite.

To determine the relative decomposing action of hydrofluoric acid on columbite and tantalite ores, a leach was conducted on a sample of columbite from Foote Mineral Company, Philadelphia. This leach was made with 100 grams of calcium fluoride and 200 cc. of sulfuric acid. Fig. 4 shows the results, compared with those from the tantalite ore.

It is evident that there is little difference in the rate of decomposition of columbite and tantalite by the use of hydrofluoric acid. Since columbium oxide is even more soluble in oxalic acid than tantalum oxide,[5]

and since the ore must be decomposed before it can be dissolved, it seems certain that all of the leaching results obtained with tantalite will be equally applicable to columbite.

LEACHING AT CONSTANT VOLUME.

Effect of Acid Concentration.

In the previous work the method of leaching was to allow the condensation of steam within the leaching solution, this steam serving as a

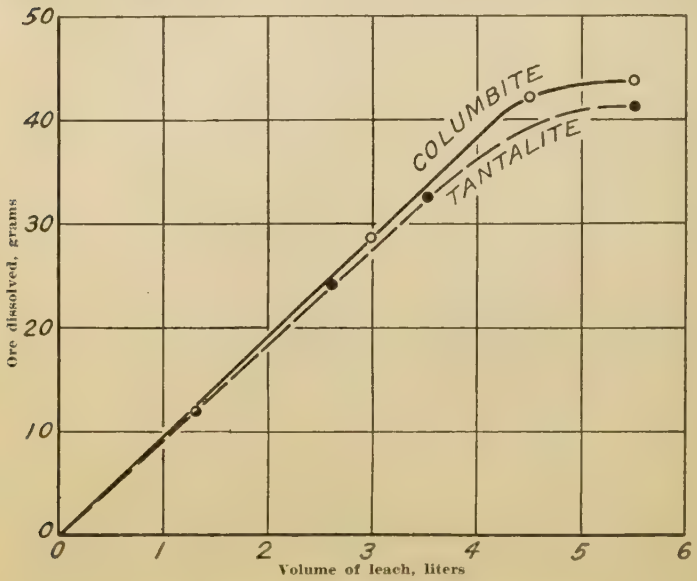

FIG. 4. Comparison of action on tantalite and columbite.

source of heat, but at the same time decreasing the concentration of the leaching reagents through dilution of the solution. The leaching curves previously considered have, as a result, three variables, time, acid concentration and amount of ore leached. Since the solution is continuously increasing in volume with time, the concentration of ore within the solution would not be expected to be in equilibrium with a given acid concentration.

A consideration of this fact would lead to the belief that if the volume of the solution is maintained constant, other conditions remaining the same, the amount of ore leachable by a given acid concentration should

be increased. With this in view, a series of constant volume leaches was conducted with several different acid concentrations, but in all cases such that the ratio of sulfuric acid to calcium fluoride to oxalic acid should be the same. This ratio was taken as 200 cc. sulfuric acid, 100 grams calcium fluoride and 155 grams of oxalic acid, the same ratio as that used in the steam condensation leach.

The apparatus employed for these experiments is shown in Fig. 5. The water in the trough was adjusted to such a level that a volume of five liters would be obtained in the pails. The pails were then filled to

TABLE II.

Cc. H_2SO_4	Grams CaF_2	Grams $H_2C_2O_4.2H_2O$
40	20	31
80	40	62
125	62.5	97
160	80	124
200	100	155
400	200	310
400	200	none

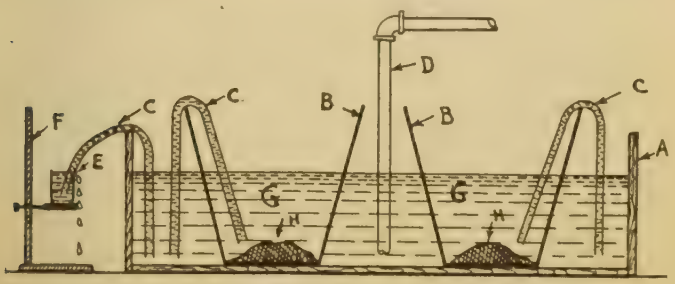

FIG. 5. Leaching at constant volume.

A—Wooden trough. B—Lead-lined pails. C—Rubber tubing. D—Steam line. E—Glass beaker. F—Ring stand. G—Acid solution. H—Ore and calcium fluoride.

about 4.5 liters with water and the desired amount of sulfuric acid. When the temperature of the solution reached its maximum, about 90° C., the ore, calcium fluoride and oxalic acid were introduced, the siphon made between the pail and the trough, and this point taken as the start of the reaction.

Samples were then removed at definite time intervals, filtered and analyzed for total oxides dissolved. This was continued until the analyses showed that no further solution of the ore was taking place. By this method, leaches were made containing the concentrations of leaching reagents as shown in Table II.

A summary of the data obtained is shown in Table III, the concentrations being given in grams per liter. In this table, as well as in further discussion, reference to the sulfuric acid concentration will assume the presence of the other leaching reagents in the same proportion as shown in Table II.

RATE OF LEACHING.

Fig. 6 shows the rate of leaching and the maximum concentration of dissolved oxides obtained, with and without the presence of oxalic acid. It is obvious that oxalic acid shows the same beneficial effect when leaching at constant volume as by the steam-dilution method. If the other results in Table III were plotted it would be found that

TABLE III.

Summary of Results Obtained in Leaches.

40 cc. H_2SO_4 per Liter.

Time Hr.	Time Min.	Ore Dissolved per liter	Time Hours	Ore Dissolved per liter
	30	3.23	20	3.98
1		3.34	22	4.15
1	30	3.62	24	4.00
3		3.27	48	4.13
3		3.60	72	4.17

80 cc. H_2SO_4 per Liter.

Time Min.	Ore Dissolved per liter	Time Hours	Ore Dissolved per liter
5	4.77	2	6.12
10	4.83	4	6.69
20	5.97	24	8.14
30	6.14	48	8.02
60	6.40		

125 cc. H_2SO_4 per Liter.

Time Hours	Ore Dissolved per liter	Time Hours	Ore Dissolved per liter
1	5.06	36	12.50
24	11.01	48	12.48

160 cc. H_2SO_4 per Liter.

Time Min.	Ore Dissolved per liter	Time Hr.	Time Min.	Ore Dissolved per liter
5	3.33	1	30	9.64
10	6.22	3	30	12.83
20	6.07	5	30	16.43
30	7.06			

TABLE III.—Continued.

200 cc. H_2SO_4 per Liter.

Time Hours	Ore Dissolved per liter	Time Hours	Ore Dissolved per liter
1	11.53	24	15.4
2	12.81	72	20.6

400 cc. H_2SO_4 per Liter.

Time Hr. Min.	Ore Dissolved per liter	Time Hr. Min.	Ore Dissolved per liter
10	10.52		28.1
20	17.6	3 30	30.0
30	2 10	24	39.5
1 10	21.8	48	40.2

400 cc. H_2SO_4 per Liter (without oxalic).

Time Min.	Ore Dissolved per liter	Time Hr Min.	Ore Dissolved per liter
10	9.02	2	19.1
20	12.5	3	22.0
30	14 1	21 30	23.1
60	15.3	25 45	23.0

they all show the same type of curves, differing only in the maximum concentration. It is also seen that this maximum concentration varies directly with the concentration of acids taken, as will be seen by referring to Fig. 8.

It is of interest to note that the rate of approaching the maximum concentration appears to be the same for all concentrations when oxalic acid is used, but different without the presence of oxalic acid. The logarithmic curves in Fig. 7 show that this rate can be represented by the equation

$$t = a(c, C)^b$$

where t = time in hours

c = conc. in g./L. of dissolved oxides at any time t

C = maximum conc. in dissolved oxides expressed as g./L.

a = constant

and b = constant.

These curves were obtained by plotting log t against log c C, the resulting curves being a straight line. When the equation for a straight line is put in the form

$$y = mx + b,$$

m is the slope of the line and b is the intercept on the Y axis. Since the logarithmic curve for the equation

$$t = a(c/C)^b$$

would be

$$\log t = b \log(c/C) + \log a$$

then b would be represented by the slope of the logarithmic curve and log a would be the value of the intercept on the log t axis. Utilizing this principle the equations were found to be $t = 3.55(c\ C)^{3.2}$ without the presence of oxalic acid and $t = 8.5(c\ C)^{3.5}$ in the presence of oxalic acid.

Although the second equation was developed from the leach using 160 cc. sulfuric acid per liter it will be seen that it applies equally as well to other leaches, since calculations show results close to those determined. This comparison is shown in Table IV.

TABLE IV.

Conc. Acid cc./liter	Conc. in Dissolved Oxides, g./L.	
	Calculated	Determined
	Concentration After 30 Minutes.	
160	7.12	7.06
400	17.8	17.6
	Concentration After 1 Hour.	
160	8.65	8.40
200	10.8	11.5
400	21.6	21.8

It is realized that there are a large number of reactions taking place during the leaching, but it is believed that the reactions governing the rate of leaching can be represented as taking place in the following manner:

(1) $FeTa_2O_6 + 12HF = 2\ TaF_5 + FeF_2 + 6H_2O.$

(2) $2TaF_5 + 5\ H_2C_2O_4 = Ta_2(C_2O_4)_5 + 10HF.$

It may, however, be somewhat questionable as to the formation of a true oxalate, but a reaction similar to this must take place. It is also understood that columbium and manganese may replace the tantalum and iron respectively in the above reactions.

The first equation developed, $t = 3.55(c\ C)^{3.2}$, would represent the first reaction above, while the second equation, $t = 8.5(c\ C)^{3.5}$ would represent the summation of the two reactions. It is evident, that the decomposing reaction takes place at a faster rate than does the transfer to the oxalate.

COMPARISON OF RESULTS BY THE TWO LEACHING METHODS.

By comparing the concentration of dissolved oxides for a given acid concentration by the two methods of leaching, Fig. 8, it will be observed that the steam-dilution method is far superior to the constant volume method. This is contrary to what might be expected, but can be explained by the fact that the hydrofluoric acid-oxalic acid solution is capable of retaining more ore in solution than can be decomposed for any given acid concentration. This fact has been constantly observed throughout the investigation, and seems to be due to the manner in which the oxalic acid functions.

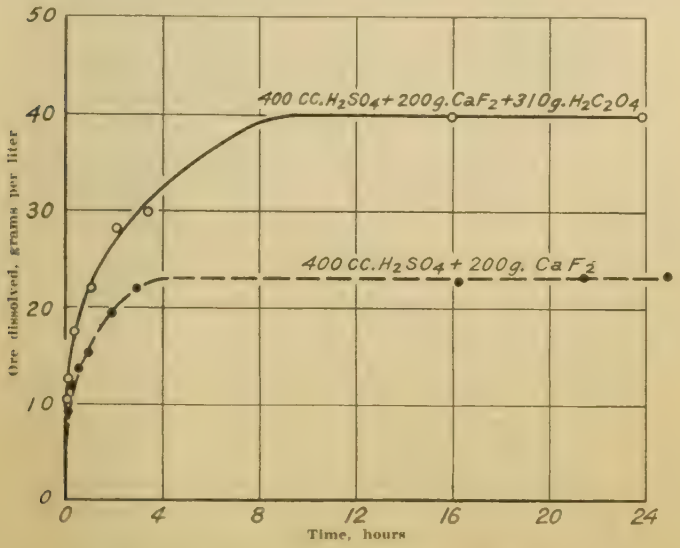

FIG. 6. Rate of leaching at constant volume.

It has been shown that the rate of decomposition of the ore is greater than the transfer to the soluble oxalate compound. It was also shown experimentally that the two reactions could not be carried out successively, and arrive at the same results obtained when allowing them to take place simultaneously. The explanation, therefore, seems to be explained by the following considerations:

1. When the reactions are taking place simultaneously the hydrofluoric acid concentration is kept higher, due to its liberation in the second reaction. Therefore, the amount of decomposition of the ore can be increased.

2. The rate of the second reaction is slower, and the maximum benefit of the oxalic acid cannot be obtained, since there is another factor to consider, the rate of volatilization of the hydrofluoric acid.

3. Best results would be obtained if the second reaction took place with at least equal speed to that of the decomposing reaction.

4. The nearest approach to this ideal condition is to allow the reaction to take place in concentrated solution, where the extent of the

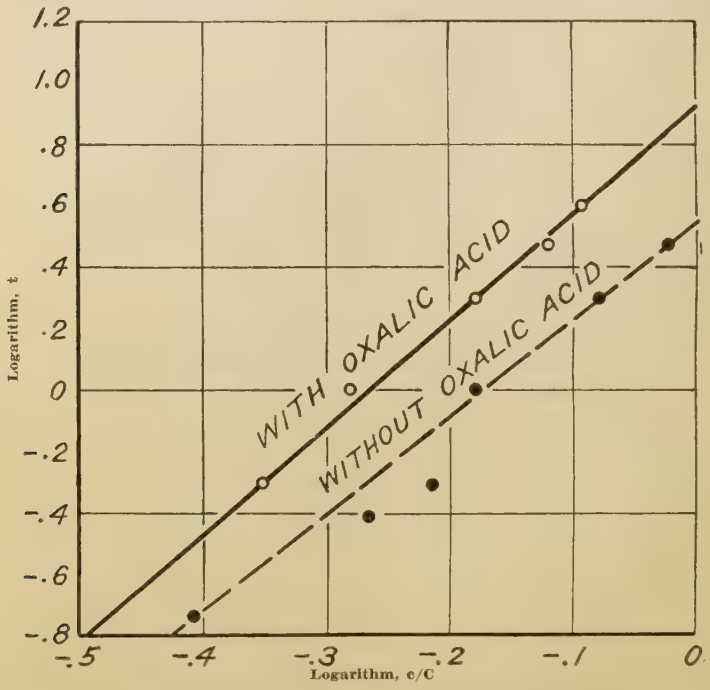

FIG. 7. Logarithmic curves. Rate of approaching limiting concentration.

reaction is greatly magnified, and to dissolve the soluble oxalate compound by dilution of the solution in the presence of free oxalic acid. This is what takes place in the steam-dilution method.

Optimum Conditions for Leaching.

The experiments showed that 155 grams of oxalic acid in five liters was practically as efficient as larger quantities, but that smaller amounts caused a drop in leaching efficiency. It is also seen that this amount

of acid will leach about three times as much ore by the steam-dilution method. The best conditions for leaching, therefore, are to use the steam-dilution method, to use a slight excess of fluorspar with the ore, and to have 200 cc. of concentrated sulfuric acid and about 150 grams of oxalic acid present for each five liters of final leaching solution.

RECOVERY OF TANTALUM AND COLUMBIUM FROM THE LEACHING SOLUTION.

Crystallization of Potassium Tantalofluoride.

The only utilized commercial method of separating tantalum from columbium is based upon the difference in solubility of tantalum and columbium double fluorides of potassium, the former being much less

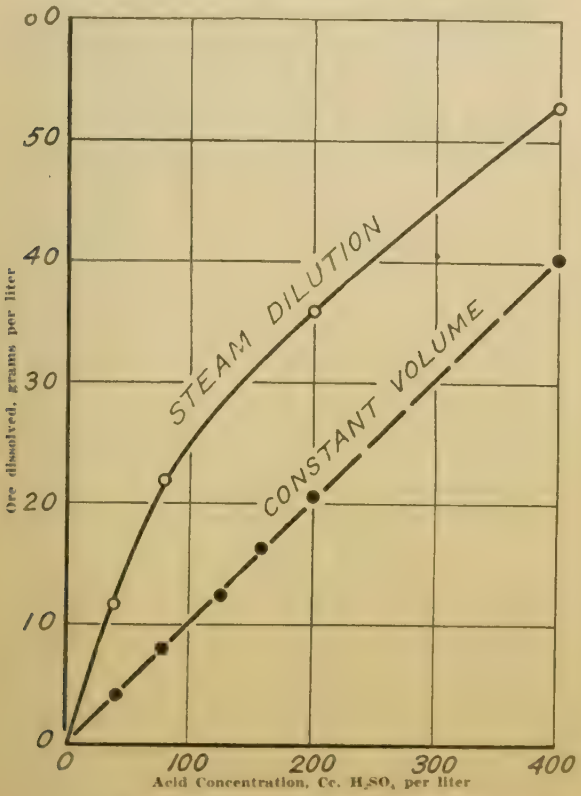

FIG. 8. Dissolved oxides as function of acid concentration.

soluble. It seemed of value, therefore, to investigate the possibility of separating the tantalum from the leaching solution by means of this principle.

For this study, a leach was conducted in a steam-jacketed, lead evaporating pan of about 19 liters capacity. A leach of 19 liters was made, which contained 190 grams of dissolved oxides. The clear solution was transferred to a second evaporating pan of the same type, heated to about 80° C., and 150 grams of potassium fluoride and 300 grams of 50 per cent hydrofluoric acid added. Considerable crystallization took place immediately, and this increased upon concentration of the solution. Some of the first crystals were removed, after which the solution was evaporated to five liters, the crystals filtered off, washed and dried over a steam radiator.

The weight of the final product was 960 grams and analyzed 7.59 per cent tantalum oxide. The presence of iron could be faintly detected with potassium sulfocyanide and manganese by the sodium carbonate-potassium chlorate bead, but both elements were present only in faint traces. The presence of columbium could not be detected by reduction with tin or by the method of Powell and Schoeller.[5] It seemed evident, therefore, that these crystals consisted of oxalic acid and potassium tantalofluoride.

On the assumption that the dissolved oxides contained 60 per cent tantalum oxide, the tantalum recovered free from columbium was about 64 per cent of that leached. It would be necessary, however, to separate the large amount of oxalic acid accompanying it. This could be done by further crystallization from hot solutions, and a recovery of considerable oxalic acid could be made.

The first crystals removed were of high purity and contained no oxalic acid. No data are available to show the per cent of recovery of the pure product, but it is certain that considerable can be recovered which will not require recrystallization.

Fractional Precipitation with Alkalies.

It was observed that tantalum and columbium could be precipitated from the leaching solution while it was still acid, and this led to an investigation of this method of recovering the oxides of these metals. An electrometric titration of the solution with ammonium hydroxide, using a quinhydrone electrode, showed precipitation to start at a pH of 1.1. Further study showed that a large amount of precipitate was obtained when adding ammonium hydroxide to the solution until basic to methyl orange, pH of 5, and considerably more when basic to methyl red, pH of 6. Neither of these precipitates showed the presence of iron

or manganese when testing with potassium sulfocyanide, and the sodium carbonate-potassium chlorate bead respectively. Experiments were then conducted to determine the efficiency of recovery and the purity of the product.

Using sodium hydroxide as the precipitant, and precipitating just to the acid side of litmus paper, a product was obtained after drying at 100° C. which was soluble in hydrochloric acid. The product contained no metals of the acid hydrogen sulfide group, no titanium, showed a faint test for iron and manganese, and contained 53.8 per cent of combined tantalum and columbium oxides. It was evident, however, that it contained a large amount of oxalate, sodium and water and appeared to be a double oxalate of the metals with sodium.

Since it was evident that the alkali would accompany the metal in the final product, it seemed advisable to use ammonium hydroxide as the precipitant, which could later be eliminated by ignition. A precipitation

TABLE V.

Weights of Products.

	Grams	Per cent
No. 1. Precipitated on acid side of litmus	32.0	86.5
No. 2. Precipitated on basic side of litmus	5.0	13.5

Analysis of No. 1.

	Per cent
Ta_2O_5	44.8
Cb_2O_5	15.2
SiO_2	0.81
TiO_2	none
H_2S (acid) metals	none
Fe_2O_3 (KCNS test)	trace
MnO_2 (Na_2CO_3-$KClO_3$ bead test)	trace
C_2O_4	16.5
NH_3	present
SO	0.33
F	present

Analysis of No. 2.

	Per cent
$Ta_2O_5 + Cb_2O_5$	6.2
SiO_2	39.9

Recovery of $Ta_2O_5 + Cb_2O_5$.

	Grams	Per cent
$Ta_2O_5 + Cb_2O_5$ in No. 1	19.2	98.5
$Ta_2O_5 + Cb_2O_5$ in No. 2	0.31	1.5

was, therefore, conducted by adding ammonium hydroxide, until the solution was just basic to litmus paper, and then sulfuric acid until it was distinctly acid to litmus paper. The precipitate was filtered off, after washing several times by decantation, and dried at 110° C. The decanted solution and washings were made basic with ammonium hydroxide, filtered, washed and dried. Each of these products was then weighed and analyzed. The results are shown in Table V.

It was evident that the tantalum and columbium could be precipitated from the acid solution in a state practically free from other metals, and with very good recovery of the metal oxides.

SELECTED METHOD FOR COMMERCIAL OPERATION.

The method utilized commercially would depend upon the product desired. For purposes where no separation of tantalum and columbium is desired, the fractional precipitation with ammonium hydroxide would be employed. The successive use of these two methods however, could be used to recover a large amount of the tantalum free from columbium and the balance with columbium.

SEMI TECHNICAL RESULTS.

For a study of the method of leaching on a larger scale it was considered advisable to utilize ores which were available in this country. The ores studied were samarskite and columbite, obtained from A. D. MacKay, New York City, the former stated to be from North Carolina and the latter from South Dakota.

Samarskite.

This ore is very troublesome to work for tantalum and columbium by present methods, as it contains uranium, cerium, yttrium, erbium and other rare earths in addition to the metals present in tantalite and columbite. The tantalum and columbium content is only 50 to 55 per cent of the ore, represented as oxides, and the yield, therefore, is much smaller for this ore. It was realized, however, that the rare earth metals should not be leached in the presence of oxalates and fluorides and could, consequently, be left in the gangue. Except for uranium, therefore, there would be no additional difficulty in working with this ore.

To verify this assumption, a 19-liter leach was made on this ore, using the following materials: 500 grams ore, 600 grams fluorspar, 1,200 grams oxalic acid, 1,200 cc. sulfuric acid. A volume of 18 liters obtained from the leach showed a concentration of 18.2 grams per liter of oxides precipitable with ammonia, showing a leach of 338 grams of

oxides. It is evident from these results, as well as from observations, that this ore is more easily leached than the tantalites and columbites.

The tantalum and columbium were precipitated from the solution with ammonium hydroxide, keeping the solution acid to litmus, washed by decantation and finally filtered. A sample dried at 110° C. showed the following analysis:

	Per cent
Loss on ignition	36.5
$Ta_2O_5 + Cb_2O_5$	55.0
Fe_2O_3	trace
MnO_2	trace
NH_3	present
UO_3	present
Rare earths	none
C_2O_4 (oxalate)	24.1
SO_3	0.20
SiO_2	1.6

Although no further work was done with this ore, it is believed that the uranium could be removed by leaching the precipitated oxides with ammonium carbonate.

Columbite.

This ore was reduced from the lump to a 50-mesh material by passing through a jaw crusher and set of rolls, the 50-mesh ore then being used for the leach. The leach was conducted in a 189-liter, lead-lined tank by the steam-dilution method, the charge consisting of 6 lb. (2.7 kg.) of ore; 10 lb. (4.5 kg.) fluorspar; 12 lb. (5.4 kg.) oxalic acid; 32 lb. (14.5 kg.) 66° Be sulfuric acid; 19 liters of water.

Steam was introduced through a rubber hose, and the leach conducted over a period of five hours, a final volume of 189 liters being obtained. The solution was allowed to settle over night, and the clear solution then transferred to a wooden tank for precipitation.

The wooden tank had a diameter of two feet (0.61 m.) one inch (2.5 cm.) of depth, containing 1.955 gallons (7.4 L). The tank was filled to a depth of 23 inches (58.4 cm.), representing 45 gallons (170 L.) of solution. This volume was nine-tenths of the leach, the balance being saved for other investigations. The oxides were precipitated with 26° Be ammonium hydroxide to the acid side of litmus paper, 40 pounds (18.3 kg.) being required. The precipitate was washed twice by decantation and filtered.

Since it was desired to use these oxides for further investigations, and since drying rendered them less soluble, a sample was analyzed for purity, and the balance stored in well stoppered bottles. The yield was then obtained by determining the total oxides leached and the oxides not

precipitated by ammonia on the acid side of litmus. The results are shown in Table VI

The sample dried at 110° C. showed 1.3 per cent silica, and faint traces of iron and manganese. It would be concluded, therefore, that about 3.5 lb. (1.6 kg.) of combined tantalum and columbium oxides could be recovered after calcining the product.

TABLE VI.

Concentration of leaching solution in total oxides	10.9 g./L.
Total oxides in 189 liters solution	2.06 kg.
Volume of solution after precipitation	191.5 L.
Concentration of solution after precipitation in total oxides	1.83 g./L.
Total oxides not precipitated from 153 liters	3.35 kg.
Total oxides not precipitated from 189 liters	0.39 kg.
Total oxides precipitated from 189 liters	1.67 kg.

COST CALCULATIONS.

On the basis of the semi technical results, the cost of the materials consumed for the production of one pound (0.45 kg.) of the combined oxides of tantalum and columbium would be

10 lb. fluorspar at 1 cent per lb.	$0.10
12 lb. oxalic acid at 11 cents per lb.	1.32
32 lb. 66° Be. sulfuric acid at 0.8 cent per lb.	0.26
40 lb. 26° Be. ammonia at 3 cents per lb.	1.20
Total cost for 3.5 lb. oxides	$2.88
Cost per lb. of oxides	0.82

The apparatus employed would be of a simple type, consisting of wooden and lead-lined tanks. The cost of production, therefore, would depend largely upon the value of the ore worked, whether a separation of tantalum from columbium was made, and whether oxalic acid was recovered from the solution.

Since the cost of materials for leaching is only 48 cents per pound of combined oxides, and since it has been shown that at least 60 per cent of the tantalum can be recovered directly from the leach in the form of potassium tantalofluoride, this would place the cost of leaching the recovered tantalum oxide at $1.14 per pound. Assuming only a 50 per cent recovery of the oxalic acid during crystallization, the cost would be reduced to 63 cents per pound for the materials. It seems fair to estimate, therefore, that a pure grade of tantalum oxide could be produced commercially at a cost of $2.00 per pound, and that this would make no allowance for an equivalent quantity of the combined oxides which could be recovered from the solution at a considerably cheaper

cost. In view of the fact that it is difficult to procure an appreciable quantity of tantalum oxide on the market, even at a price of $30 per pound, it would seem that this method warranted consideration.

SUMMARY AND CONCLUSIONS.

A method of leaching tantalum and columbium ores has been developed and the optimum conditions determined. Study has been devoted to the recovery of tantalum in the form of potassium tantalofluoride and to the recovery of the combined oxides of tantalum and columbium from the solution after leaching. Tantalite, columbite and samarskite ores were studied. It was concluded from the work that

1. Hydrofluoric acid acts as a good decomposing agent for the tantalum and columbium ores.

2. The presence of carboxylic acids greatly increases the rate of decomposition and solution of the ore.

3. The effectiveness of the carboxylic group decreases with increased molecular weight of the acid containing the group, oxalic acid being by far the most efficient.

4. Hydrofluoric acid can be produced during the leaching, by employing fluorspar and sulfuric acid.

5. The combination of hydrofluoric and oxalic acids is capable of retaining more tantalum and columbium in solution than it can decompose from the ore at a given acid concentration.

6. This makes it more feasible to start with a high concentration of acids and utilize steam condensation for heating and diluting the solution.

7. The quantity of materials selected for leaching should be such that a slight excess of fluorspar is present, and 30 grams of oxalic acid and 40 cc. of sulfuric acid per liter of final solution.

8. About 60 per cent of the tantalum can be recovered in the form of potassium tantalofluoride directly from the solution after leaching, but the crystals will contain a large amount of oxalic acid.

9. By recrystallization of the above product, a large amount of oxalic acid can be recovered for leaching, and a pure salt of tantalum prepared.

10. The combined oxides of tantalum and columbium can be recovered from the solution by fractional precipitation with ammonium hydroxide.

11. The cost of producing these metal oxides by this method makes the process look very attractive in view of present prices.

VITA.

Leslie George Jenness was born in Danbury, New Hampshire, on August 12, 1898; received his elementary training in the Danbury, New Hampshire, public schools and in Proctor Academy, Andover, New Hampshire; was graduated from New Hampshire University with a degree of Bachelor of Science in Chemical Engineering in 1920, and from the University of Maine with a degree of Master of Science in Chemical Engineering in 1924. He was employed by the General Electric Company in their engineering laboratories at Harrison, New Jersey, in 1920 and 1921, served as instructor in mathematics at the University of Maine in 1922-23, and as instructor in chemistry in 1923-24. From 1924 to 1928 he was an instructor in chemistry at Pratt Institute, Brooklyn, New York, and has been in charge of technical chemistry in that institution since 1928. He entered the Department of Chemical Engineering of Columbia University in June, 1924.